

COMPOSITION FOR OPTICAL WAVEGUIDE ARTICLE AND METHOD FOR MAKING CONTINUOUS CLAD FILAMENT**Publication number:** WO9858884**Publication date:** 1998-12-30**Inventor:** CHU POLLY W; DEJNEKA MATTHEW J; TYNDELL BRIAN P; YOST KEVIN J**Applicant:** CORNING INC (US)**Classification:****- international:** C03B37/012; C03B37/023; C03B37/026; C03B37/027; C03C13/04; G02B6/02; C03B37/012; C03B37/02; C03C13/00; G02B6/02; (IPC1-7): C03C13/04; C03B37/023; G02B6/02**- european:** C03B37/012B; C03B37/012D; C03B37/023; C03B37/026; C03B37/027; C03C13/04D2; G02B6/16**Application number:** WO1998US12336 19980611**Priority number(s):** US19970050469P 19970623**Also published as:**

EP1015396 (A1)
EP1015396 (A0)
CA2289768 (A1)
AU743385 (B2)

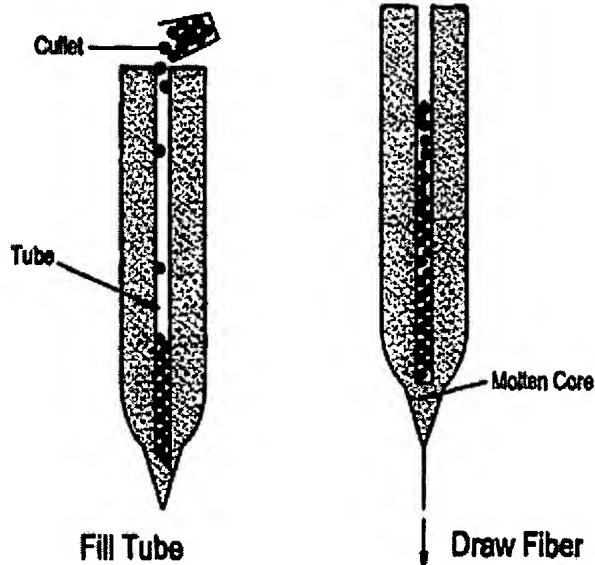
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Abstract of WO9858884

An optical article having a rare earth doped, fluorinated aluminosilicate glass core composition consisting essentially, in mole %, of: SiO₂ 0-90; GeO₂ 0-90; Na₂O 0-25; Li₂O 0-10; K₂O 0-25; Rb₂O 0-25; Cs₂O 0-25; Al₂O₃ 5-40; Ga₂O₃ 5-40; RE₂(1)O₃ 0-40; RE₂(2)O₃ 0-1; Er₂O₃ 0.001-5; Yb₂O₃ 0-5; PbO 0-15; RO 0-20; ZnO 0-10; ZrO₂ 0-2; TiO₂ 0-2; Nb₂O₅ 0-10; Ta₂O₅ 0-10; P₂O₅ 0-5; B₂O₃ 0-15; As₂O₃ 0-10; Sb₂O₃ 0-20; Na₂Cl₂ 0-10; Bi₂O₃ 0-5, and up to 15 weight % fluorine in the form of at least one of a fluorinated component of the glass composition and a batch constituent selected from a group consisting of at least one of AlF₃, RE₃F₃, NH₅F₂, NaF, Na₂SiF₆, Na₃AlF₆.



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(51) International Patent Classification ⁶ : C03C 13/04, C03B 37/023, G02B 6/02	A1	(11) International Publication Number: WO 98/58884 (43) International Publication Date: 30 December 1998 (30.12.98)
(21) International Application Number: PCT/US98/12336 (22) International Filing Date: 11 June 1998 (11.06.98) (30) Priority Data: 60/050,469 23 June 1997 (23.06.97) US (71) Applicant: CORNING INCORPORATED [US/US]; 1 Riverfront Plaza, Corning, NY 14831 (US). (72) Inventors: CHU, Polly, W.; 108 Weston Lane, Painted Post, NY 14870 (US). DEJNEKA, Matthew, J.; 10 Ellison Road, Corning, NY 14830 (US). TYNDELL, Brian, P.; 10 Maple Street, Addison, NY 14801 (US). YOST, Kevin, J.; 561 Victory Highway, Painted Post, NY 14870 (US). (74) Agents: HERZFELD, Alexander, R. et al.; Corning Incorporated, Patent Dept., SP FR 02-12, Corning, NY 14831 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: COMPOSITION FOR OPTICAL WAVEGUIDE ARTICLE AND METHOD FOR MAKING CONTINUOUS CLAD FILAMENT		
(57) Abstract <p>An optical article having a rare earth doped, fluorinated aluminosilicate glass core composition consisting essentially, in mole %, of: SiO₂ 0-90; GeO₂ 0-90; Na₂O 0-25; Li₂O 0-10; K₂O 0-25; Rb₂O 0-25; Cs₂O 0-25; Al₂O₃ 5-40; Ga₂O₃ 5-40; RE₂(1)O₃ 0-40; RE₂(2)O₃ 0-1; Er₂O₃ 0.001-5; Yb₂O₃ 0-5; PbO 0-15; RO 0-20; ZnO 0-10; ZrO₂ 0-2; TiO₂ 0-2; Nb₂O₅ 0-10; Ta₂O₅ 0-10; P₂O₅ 0-5; B₂O₃ 0-15; As₂O₃ 0-10; Sb₂O₃ 0-20; Na₂Cl₂ 0-10; Bi₂O₃ 0-5, and up to 15 weight % fluorine in the form of at least one of a fluorinated component of the glass composition and a batch constituent selected from a group consisting of at least one of AlF₃, REF₃, NH₅F₂, NaF, Na₂SiF₆, Na₃AlF₆.</p> <div data-bbox="649 1155 1380 1848"><p>The diagram consists of two vertical cross-sectional views of a glass tube. The left view, labeled 'Fill Tube', shows a tube with a central core. A 'Cullet' (a small piece of glass) is shown being added to the top of the tube. The right view, labeled 'Draw Fiber', shows the same tube with a 'Molten Core' at the bottom, from which a fiber is being drawn downwards, indicated by a downward arrow.</p></div>		

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**COMPOSITION FOR OPTICAL WAVEGUIDE ARTICLE
AND METHOD FOR MAKING CONTINUOUS CLAD FILAMENT**

Background of the Invention

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Field of the Invention

This invention relates to a novel core glass composition that is particularly suited for, but not limited to, optical waveguiding signal amplifier articles due, in part, to the flatness of its gain spectrum; and to a non-CVD method for making continuous clad filaments. More particularly, the invention relates to a novel rare earth doped, fluorinated aluminosilicate glass composition and to a cullet-in-tube method for making continuous clad filament such as, e.g., optical waveguiding fiber and conductive conduit.

10

Description of Related Art

This application is related to provisional U.S. application serial number 60/034472, filed on 01/02/97, which is herein incorporated by reference in its entirety.

15

Erbium doped optical amplifiers and, in particular, erbium doped fiber amplifiers, have revolutionized optical telecommunications by providing all optical high gain, low noise amplification without the need for costly repeaters. Current erbium doped fiber amplifiers, however, are not well suited for multi-channel amplification due to the variation of their gain spectrum as a function

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of wavelength, denoting gain flatness or the lack thereof. As used herein, the term "gain flatness" will refer to the change in the shape of the gain spectrum over a particular wavelength range; i.e., flat gain means substantially equal gain for all wavelengths over the wavelength range of interest. For erbium, the wavelength range of interest is from about 1530 nm to 1560 nm. When the gain spectrum is not sufficiently flat over this wavelength interval, multiple channels at different wavelengths are not uniformly amplified, making high data rate communication systems inoperable, impractical and unaffordable.

The art teaches that co-doping an erbium doped fiber with Al_2O_3 increases Er solubility and results in a flatter gain spectrum than that exhibited by an erbium doped pure silica fiber. However, currently known erbium doped aluminosilicate compositions yield a best performance gain flatness of about 27 dB of gain deviation per 100 dB of gain over a 32 nm wide band, and are prone to devitrification at high levels, i.e., greater than a few weight percent of Al_2O_3 . Compositions of SiO_2 doped with La_2O_3 or $\text{La}_2\text{O}_3 + \text{Al}_2\text{O}_3$ have also shown improved gain flatness and rare earth solubility, but the Al_2O_3 and La_2O_3 concentrations are all well below 1%, and thus have but a minor effect.

Fluoride glasses, e.g., ZBLAN ($57\text{ZrF}_4 - 20\text{BaF}_2 - 4\text{LaF}_3 - 3\text{AlF}_3 - 20\text{NaF}$ (mole %)) exhibit good gain flatness and low phonon energy, but these compositions require pumping at 1480 nm due to up-conversion effects, and exhibit increased noise over 980 nm pumping. Moreover, they are difficult to fiberize, are not fusion spliceable to silica fibers, are prone to devitrification, and have poor durability.

In addition to gain flatness, the gain provided by a rare earth doped host medium is also a parameter of interest. Higher gains can theoretically be achieved by increasing the concentration of the suitable rare earth dopant; however, above a modest concentration, rare earth ion clustering and concentration quenching become a problem. Current CVD methods for glass fiber preform fabrication are quite limited by the composition ranges of the host glasses. Only modest amounts of rare earth elements can be incorporated without clustering effects, and volatile components such as alkalis and halogens cannot

be introduced because of their tendency to vaporize during laydown. Furthermore, other important glass modifiers, e.g., alkaline earths, cannot be incorporated due to lack of high vapor pressure CVD precursors. Even if a glass soot can be deposited by CVD, it must subsequently be consolidated which can lead to crystallization or loss of glass components with high vapor pressures.

The inventors have therefore recognized a need for a glass composition and optical waveguide articles made therefrom that accommodate high levels of rare earth doping without clustering to provide high gain; that provide an improvement in gain flatness over conventional compositions; that are pumpable at 980 nm for good noise performance; that are fusion spliceable to conventional silica based fibers; that match or exceed the durability of conventional optical fiber waveguides; and that are easy to fabricate. Related application serial number 60/034472 describes a novel glass-ceramic composition and devices made therefrom that exhibits many of the advantageous requirements described above. The inventors have discovered, however, that the composition of the instant invention provides those advantages while eliminating the additional ceraming step required to make the glass-ceramic, and further provides a wider constituent composition range.

Accordingly, there is a need for a method for making waveguiding optical fiber from a wide variety of glass and glass-ceramic compositions, and other continuous clad filament articles such as, e.g., conductive conduit, that overcomes the disadvantages of the known methods, and that is more practical, efficient, and economical than conventional methods. The "cullet-in-tube" method of the invention allows almost any glass that can be produced by chemical (sol-gel, vapor deposition, etc.) or physical (batch and melt) techniques, or other feedstock in granular or powder form ("cullet" as referred to herein), to be economically fabricated in the form of a continuous clad filament. The rapid quenching of this technique allows for unstable glasses and glass-ceramics to be fiberized.

Summary of the Invention

To achieve these and other advantages and in accordance with the purpose of the invention, as embodied and broadly described, an embodiment of the invention is directed to an optical waveguiding device including a rare earth doped, fluorinated aluminosilicate glass core composition.

In an embodiment of the invention, the core composition consists essentially, in mole %, of:

10	SiO ₂	0-90
	GeO ₂	0-90
	Na ₂ O	0-25
	Li ₂ O	0-10
	K ₂ O	0-25
15	Rb ₂ O	0-25
	Cs ₂ O	0-25
	Al ₂ O ₃	0-40
	Ga ₂ O ₃	0-40
	RE ₂ (1)O ₃	0-40
20	RE ₂ (2)O ₃	0-1
	Er ₂ O ₃	0.001-5
	Yb ₂ O ₃	0-5
	PbO	0-15
	RO	0-20
25	ZnO	0-10
	ZrO ₂	0-2
	TiO ₂	0-2
	Nb ₂ O ₅	0-10
	Ta ₂ O ₅	0-10
30	P ₂ O ₅	0-5
	B ₂ O ₃	0-15

As ₂ O ₃	0-10
Sb ₂ O ₃	0-20
Bi ₂ O ₃	0-5
Na ₂ Cl ₂	0-10, and

5 up to 15 weight % fluorine in the form of a fluorinated component of the glass composition,

where RE(1) is Y³⁺ and/or La³⁺ and/or Gd³⁺ and/or Lu³⁺; RE(2) is Ce³⁺ and/or Pr³⁺ and/or Nd³⁺ and/or Sm³⁺ and/or Eu³⁺ and/or Tb³⁺ and/or Dy³⁺ and/or Ho³⁺ and/or Tm³⁺; R is Ba and/or Ca and/or Mg and/or Sr; (SiO₂ + GeO₂) is between 40-90 % mole; and
 10 the amount of (Al₂O₃ + Ga₂O₃) > (RO + "alk"₂O + RE₂O₃), where "alk" is Li and/or Na and/or K and/or Rb and/or Cs.

In an embodiment of the invention, the fluorine can be batched as one or more of the following: AlF₃, RE₂F₃, NH₄F₂, NaF, Na₂SiF₆, Na₃AlF₆.

15

In another embodiment of the invention, the optical waveguiding device has a core region consisting essentially of the composition described above and a cladding region of silicate glass adjacent the core. In an aspect of this embodiment, the cladding composition consists essentially, in mole %, of:

20	SiO ₂	90-100
	B ₂ O ₃	0-10
	P ₂ O ₅	0-10
	Al ₂ O ₃	0-10
	GeO ₂	0-10, and
25	SiF ₄	0-10.

In related aspects of this embodiment, the waveguiding device is a low loss, single mode or multimode optical fiber waveguide.

30 In another aspect of this embodiment, the waveguiding device is a rare earth doped optical fiber component of a fiber optical amplifier which exhibits a gain flatness of less

than 17 dB gain variation per 100 dB gain over a 32 nm band when pumped by an appropriate excitation source, and preferably a gain variation between about 2-16 dB/100 dB gain over selected wavelength bands between about 1525 - 1565 nm.

5 In a further embodiment, the invention is directed to a non-CVD, "cullet-in-tube" method for making a continuous clad filament, that involves filling a cladding tube that is chemically compatible with a core composition, with a core feedstock consisting of cullet of the desired, finished core composition having a particle size of between about 100 - 5,000 μm , in which the cladding tube composition is more refractory than the core
10 composition (i.e., having a softening point that is greater than the melting point of the core composition), heating an end of the tube to near its softening temperature in a furnace whereby the core composition within the tube is melted, and elongating the tube so as to draw filament therefrom. Preferably, the feedstock will have the core composition described above and a silicate cladding composition. In an aspect of this
15 embodiment, the feedstock will be cullet of conductive conduit, e.g., a superconducting composition. Cladding compositions may include, e.g., silica, calcium aluminate glass, Pyrex®.

It will be appreciated by those skilled in the art that the cullet-in-tube method
20 embodiment disclosed herein provides for making axially graded or axially-hybrid core filaments by introducing core cullet of selected compositions into the cladding tube. This process allows for the manufacture of a continuous clad filament having axially varying parameters of interest (e.g., refractive index). Such a product could take the non-limited form of, e.g., a hybrid doped active fiber for fiber amplifier applications.

25 Additional features and advantages of the invention will be set forth in the description which follows, and in part will be apparent from the description, or may be learned by practice of the invention. The objectives and other advantages of the invention will be realized and attained by the apparatus and method particularly pointed out in the written
30 description and claims hereof as well as the appended drawings.

It is to be understood that both the foregoing general description and the following detailed description are exemplary and are intended to provide further explanation of the invention as claimed. The accompanying drawings are included to provide a further understanding of the invention and are incorporated in, and constitute a part of, this specification; illustrate embodiments of the invention; and together with the description
5 serve to explain the principles of the invention.

Brief Description of the Drawings

Figure 1 shows the optimized 32 nm bandwidth gain curves for an exemplary
10 composition embodiment of the invention (heavy line) and that of conventional alumina-doped silica (light line) with the optimized band highlighted;

Figure 2 is a plot of loss (attenuation) versus wavelength for a fiber waveguide
15 according to an embodiment of the invention.

Figure 3 shows a plot of refractive index delta versus radial distance from core center for a multimode fiber waveguide embodiment of the invention;

20 Figure 4 shows a plot of refractive index delta versus radial position from core center for a single mode fiber waveguide embodiment of the invention;

Figure 5 is a schematic illustration of a cullet and tube fiberization method according to an embodiment of the invention.
25

Detailed Description of a Preferred Embodiment of the Invention

A preferred embodiment of the invention is directed to an optical waveguiding device having a new rare earth doped, fluorinated aluminosilicate glass core composition, and to a non-CVD method for making a waveguiding optical fiber having the inventive core
30 composition and a silicate glass cladding.

Reference will now be made in detail to the present preferred embodiments of the invention, examples of which are illustrated in the accompanying drawings and tables presented herein.

5 In a preferred embodiment of the invention, an optical article has a glass composition consisting essentially, in mole %, of:

	SiO ₂	60-85
	GeO ₂	0-5
	Na ₂ O	3-15
10	Li ₂ O	0-10
	K ₂ O	3-15
	Al ₂ O ₃	8-27
	Ga ₂ O ₃	0-5
	RE ₂ (1)O ₃	0-40
15	Er ₂ O ₃	0.002-0.1
	Yb ₂ O ₃	0-1
	PbO	0-10
	RO	0-15
	ZnO	0-5
20	Ta ₂ O ₅	0-2
	B ₂ O ₃	0-2
	As ₂ O ₃	0-2
	Sb ₂ O ₃	0-2
	Na ₂ Cl ₂	0-4, and

25 up to 15 weight % fluorine in the form of a fluorinated component of the glass composition,

where RE(1) is Y³⁺ and/or La³⁺ and/or Gd³⁺ and/or Lu³⁺; R is Ba and/or Ca and/or Mg and/or Sr; (SiO₂ + GeO₂) is between 60-85 mole %; and the amount of (Al₂O₃ + Ga₂O₃) > (RO + "alk"₂O + RE₂O₃) where "alk" is Li and/or Na and/or K and/or Rb and/or Cs.

In a preferred embodiment of the invention, the optical article is an optical fiber waveguiding device such as the active fiber component of a fiber optical amplifier, for example, having a core composition as described above and a silicate glass cladding. In an aspect of this embodiment, the cladding consists essentially, in mole %, of:

5	SiO ₂	90-100
	B ₂ O ₃	0-10
	P ₂ O ₅	0-10
	Al ₂ O ₃	0-10
	GeO ₂	0-10, and
10	SiF ₄	0-10.

Table I shows exemplary core glass compositions (all normalized to 100%, and all in mole % amounts), according to embodiments of the invention.

Table I

e.g.	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
SiO ₂	51.01	64.06	75.54	62.78	63.59	59.91	40.86	56.34	69.95	69.94	68.86	70.19
Na ₂ O	11.19	5.525	3.777	4.484	5.53	5.53	6.452	7.512	4.664	4.663	6.12	3.275
Al ₂ O ₃	29.08	21.64	15.11	21.26	22.12	22.12	28.41	20.66	18.65	18.65	16.07	18.25
Al ₂ F ₆	0.459	0.46	0	0.269	0	0	0.448	0	0	0	2.30	0
La ₂ F ₆	7.798	7.459	5.099	7.175	7.373	7.373	7.706	5.634	6.716	6.715	6.61	6.373
Er ₂ F ₃	0.459	0.46	0.472	0.448	0.461	0.461	0.448	0.469	0.013	0.026	0.05	0.047
PbO	0	0	0	0	0	0	6.72	0	0	0	0	0
BaO	0	0	0	3.587	0	0	0	0	0	0	0	0
TiO ₂	0	0	0	0	0.922	0	0	0	0	0	0	0
Ta ₂ O ₅	0	0	0	0	0	4.608	0	0	0	0	0	0
B ₂ O ₃	0	0	0	0	0	0	8.961	9.39	0	0	0	0
NaCl	0	0	0	0	0	0	0	0	0	0	0	1.872

5

The chemical composition of the glass can be varied over a large range to engineer both physical and optical properties as well as gain flatness for the specific application. SiO₂ is the main glass former, with greater SiO₂ levels leading to greater glass stability, viscosity, and compatibility with conventional fibers (i.e., SiO₂ based fibers), while decreasing the coefficient of thermal expansion, refractive index, density, and liquidus temperature. As the amount of SiO₂ in the glass increases, the Er³⁺ emission approaches that of conventional Er amplifiers and exhibits less gain flatness. As in most optical glasses, GeO₂ has the same role as SiO₂ and can be fully substituted for SiO₂ to increase the index of refraction.

15

To optimize gain flatness, the composition should contain more ($\text{Al}_2\text{O}_3 + \text{Ga}_2\text{O}_3$) than (“alk”₂O+RO+RE₂O₃), otherwise an alkali silicate-like Er³⁺ emission spectra will result, leading to a narrow and irregular gain spectrum. Fluorine is key to further smoothing of the gain spectrum and is also useful for drying the glass and maintaining a low refractive index for compatibility with conventional fibers. Between 2 and 50% of the batched fluorine can be lost during melting depending on composition, fluorine source, and melting time and temperature. Crucible lids, low humidity, dry batch materials, and low melting temperatures help minimize these losses. The fluorine can be batched as AlF₃, RE₃F₃, NH₃F₂, NaF, Na₂SiF₆, Na₃AlF₆, or any other fluorinated component of the composition, up to 15 weight %.

The “alk”₂O and RO components increase the thermal expansion and fluorine retention, and decrease the RE solubility. Their amounts and identities can be used to tailor refractive index in the manner known to those skilled in the art. They also serve to decrease the liquidus temperature of the glass making it more stable towards devitrification. PbO increases the refractive index and decreases the liquidus. Other minor components such as ZrO₂, TiO₂, Nb₂O₅, and Ta₂O₅ can also be added to the glass to increase the refractive index.

B₂O₃ decreases the density of the glass, but it also lowers the Er³⁺ fluorescence lifetime when added in significant amounts, so it is preferably used sparingly. The usual fining agents, As₂O₃ and Sb₂O₃, can be incorporated without altering the effectiveness of the material. Chloride fining agents can also be used and have the added benefit of drying the glass. The glass must be kept dry to prevent quenching of the Er³⁺ via O-H phonons.

The inventive glass composition has high rare earth (RE) solubility, a high degree of gain flatness, and provides superior Er³⁺ performance at 1550 nm. Gain flatness variations of less than 17 dB/100 dB of gain were achieved between 1530 to 1562 nm, with less than 4 dB of noise, in a 4.7 m fiber amplifier utilizing an active fiber waveguide according to an embodiment of the invention. More than 20 dB of gain was achieved with 95 mW of pump power at 980 nm. The glass modifiers are believed to be the key

- to obtaining the flat Er^{3+} gain spectra. High levels (> 1 mole %) of Al_2O_3 , RE_2O_3 ($\text{RE} = \text{Y}^{3+}$, La^{3+} , Gd^{3+} , and Lu^{3+}), and F allegedly increase the intensity of the Er^{3+} emission around 1540 nm while suppressing the emission at 1530 nm relative to the long wavelength emission (> 1540 nm), thus providing a gain spectrum as shown in Fig. 1.
- 5 Preferably, Al_2O_3 concentrations will be greater than 5 mole % and SiO_2 will be below 90 mole % to avoid the liquid-liquid immiscibility gap in the SiO_2 - Al_2O_3 - RE_2O_3 system. Other optional modifiers such as alkali and alkaline earth oxides will further alter the Er^{3+} gain spectrum and can suppress the immiscibility
- 10 Various optical articles having rare earth doped, fluorinated aluminosilicate glass cores according to embodiments of the invention have been fiberized with both borosilicate and pure silica claddings. Low loss fibers having attenuation between about 0.30 - 0.75 dB/m at 1310 nm, as represented in Fig. 2, have been made in multimode configurations as depicted in Fig. 3 and in single mode configurations as shown in Fig. 4. Refractive
- 15 index deltas between 0.6 and 2.1 % have been achieved as represented in Fig's 3 and 4.
- In an exemplary embodiment, a fiber optical amplifier comprising an active fiber according to an embodiment of the invention (Table I, e.g. XI) was constructed. The active fiber had an Er^{3+} concentration of 1.62×10^{20} ions/cc and exhibited a gain of 18
- 20 dB over 0.18 m of fiber. The fiber amplifier had a gain flatness variation of less than 20 dB per 100 dB of gain over the 32 nm band, as shown in Fig. 1. The fiber was fusion spliced to a conventional silica based fiber and demonstrated splice losses of 0.05 - 0.18 dB/splice.
- 25 Although the invention has thus far been described in terms of a waveguiding optical fiber for a fiber amplifier, those skilled in the art will appreciate that the optical articles contemplated by the invention may also include, but are not limited to, e.g., planar amplifiers, fiber lasers, Faraday rotators, filters, optical isolators, and nonlinear waveguiding fibers. Moreover, in conjunction with a method embodiment of the
- 30 invention to be described below, the fabrication of continuous clad filaments for conductive conduit is contemplated, resulting in, e.g., superconducting wire. Electro-optical composites are also envisaged.

A method embodiment of the invention is described for making a continuous-clad filament, preferably an optical waveguiding fiber, having an elongated core region of the novel glass composition described herein and a silicate glass cladding adjacent the core region, comprising the steps of a) providing a core feedstock in the form of finished
5 cullet having a particle size in the range of about 100 - 5,000 μm ; b) providing a rigid cladding structure, preferably in the form of a tube, that is chemically compatible with the core composition and is more refractory than the core composition; c) introducing the cullet into the cladding structure; d) heating an end of the core/cladding in a furnace
10 to near the softening point of the cladding; and f) drawing the core containing cladding into a continuous clad filament. The term "finished cullet" herein refers to the ultimate or final core article composition, e.g., the novel glass according to the invention, and not to the batch or pre-melting form of the composition.

15 Preferably, the core cullet is fabricated by conventional crucible melting, sol-gel, or other well known methods. As shown schematically in Fig. 5, the cullet is loaded into a hollow preform (cladding) tube. The composition of the cladding is preferably a silicate glass as described herein, but as will be appreciated by one skilled in the art, is essentially not limited and can range from pure SiO_2 to multicomponent glasses
20 including, e.g., calcium aluminate glass and Pyrex[®]. The core cullet preferably has a melting point below the softening point of the cladding, and the thermal expansion difference between the core and the cladding is not so large as to shatter the filament. After the cladding is filled with the core cullet it can be drawn down into cladded filament or rod for overcladding. The core cullet filled cladding tube is supported in a
25 furnace by well known means, and is heated to a sufficient temperature to soften the cladding glass for draw, and for melting and fining the core cullet. Preferably, the cladding structure is not sealed at any part thereof (this does not refer to temporarily closing off the draw end of the cladding structure if necessary) to allow for the escape of gasses or other by-products from the molten core. Preferably, the particle size of the
30 cullet is in the range of about 100 - 5,000 μm to avoid impaction and allow gas or other by-products to escape.

The "cullet-in-tube" method of the invention is advantageous over conventional or known cullet-in-tube methods for a number of reasons. Since the process starts with finished glass cullet, the material is well mixed on a molecular scale, and batch reactions are complete so off-gassing and bubble formation are minimized. The glass is already
5 fined of small seeds, and any large bubbles entrapped from the powder melting will quickly float to the top in the fluid molten core. The preferred method opens up a large range of compositions for fiberization that have not previously been attainable with CVD, MCVD or PCVD. The method also accommodates large differences in thermal expansion between the core and cladding materials since the core is not rigidly bonded
10 to the clad until it is in fiber form when the stresses due to thermal expansion mismatch are much smaller than in a rigid monolithic preform. The porous cullet also allows for atmospheric control of the melt at the drawing temperature. The pressure above the core can be controlled to regulate the core diameter, as can the draw temperature. Higher draw temperatures will lead to smaller core diameters for the same given fiber
15 OD, in contrast to conventional preforms where this ratio is fixed once the blank is fabricated. The ratio of the outer diameter (OD) to the inner diameter (ID) of the tube will be roughly the same as the fiber OD/ID although, as stated, it can be controlled by the pressure (positive or negative) applied over the molten core relative to outside the cladding tube.
20

Controlled glass composition and thermal history can be used to generate graded index profiles. When the core is molten and the cladding is softening, diffusional processes are relatively fast, thus graded index profiles can be created *in situ*.

25 It will be apparent to those skilled in the art that various modifications and variations can be made in the apparatus and method of the present invention without departing from the spirit or scope of the invention. Thus, it is intended that the present invention cover the modifications and variations of this invention provided they come within the scope of the appended claims and their equivalents.

I Claim:

1. An optical article having a glass composition consisting essentially, in mole %, of:

	SiO ₂	0-90
5	GeO ₂	0-90
	Na ₂ O	0-25
	Li ₂ O	0-10
	K ₂ O	0-25
	Rb ₂ O	0-25
10	Cs ₂ O	0-25
	Al ₂ O ₃	5-40
	Ga ₂ O ₃	5-40
	RE ₂ (1)O ₃	0-40
	RE ₂ (2)O ₃	0-1
15	Er ₂ O ₃	0.001-5
	Yb ₂ O ₃	0-5
	PbO	0-15
	RO	0-20
	ZnO	0-10
20	ZrO ₂	0-2
	TiO ₂	0-2
	Nb ₂ O ₅	0-10
	Ta ₂ O ₅	0-10
	P ₂ O ₅	0-5
25	B ₂ O ₃	0-15
	As ₂ O ₃	0-10
	Sb ₂ O ₃	0-20
	Na ₂ Cl ₂	0-10
	Bi ₂ O ₃	0-5, and

30 up to 15 weight % fluorine in the form of at least one of a fluorinated component of the glass composition and a batch constituent selected from a group consisting of at least one of AlF₃, RE₃, NH₃F₂, NaF, Na₂SiF₆, Na₃AlF₆,

16

where RE(1) is at least one of Y, La, Gd, and Lu;

RE(2) is at least one of Ce, Pr, Nd, Sm, Eu, Tb, Dy, Ho, and Tm;

R is at least one of Ba, Ca, Mg, and Sr;

(SiO₂ + GeO₂) is in the range (40-90); and

5 (Al₂O₃ + Ga₂O₃) > (RO + "alk"₂O + RE₂O₃) where "alk" is at least one of Li, Na, K, Cs, and Rb.

2. The article of claim 1 wherein the SiO₂ is < 90 mole %, the Al₂O₃ is > 5 mole %, and the B₂O₃ is < 5 mole %.

10

3. The article of claim 1, comprising a core region of said glass composition; and a cladding comprising a silicate glass adjacent said core.

4. The article of claim 3 in which the cladding has a composition consisting essentially, in mole %, of:

15

SiO ₂	90-100
B ₂ O ₃	0-10
P ₂ O ₅	0-10
Al ₂ O ₃	0-10
20 GeO ₂	0-10
SiF ₄	0-10.

5. The article of claim 3 in which said article is an optical waveguiding fiber.

25 6. The article of claim 5 in which said waveguiding fiber has a loss ≤ 0.75 dB/m at 1310 nm.

7. The article of claim 5 wherein said waveguiding fiber is fusion spliceable to a conventional silica based fiber with a splice loss ≤ 0.18 dB/splice.

30

8. The article of claim 5 wherein said waveguiding fiber is a single mode fiber.

9. The article of claim 5 in which said waveguiding fiber is a gain medium for an optical signal in a given wavelength range, exhibiting a signal gain spectrum over said wavelength range when said medium is pumped by an excitation source, said gain spectrum having a gain variation of < 17 dB/100 dB gain between 1530 - 1562 nm.

5

10. The article of claim 9 in which said gain spectrum has a gain variation in the range from 2-16 dB/100 dB gain over a selected wavelength region in a wavelength band from about 1525 - 1565 nm.

10

11. The article of claim 3 in which said article is a planar waveguiding device.

12. A method for making a continuous-clad filament including a core and a cladding adjacent said core region, comprising the steps of:

a) providing a core cullet feedstock having a particle diameter between about 100 - 5,000 μm and a known melting point;

b) providing a rigid cladding structure having a softening point higher than the melting point of said core feedstock, wherein said cladding has a composition that is chemically compatible with said core;

c) introducing said cullet into said cladding structure;

d) heating an end of said core containing cladding structure in a furnace to near the softening point of said cladding; and

e) drawing said core containing cladding into a continuous clad filament.

13. The method of claim 12 in which the core cullet is a glass having a composition consisting essentially, in mole %, of:

SiO ₂	0-90
GeO ₂	0-90
Na ₂ O	0-25
Li ₂ O	0-10
K ₂ O	0-25
Rb ₂ O	0-25
Cs ₂ O	0-25

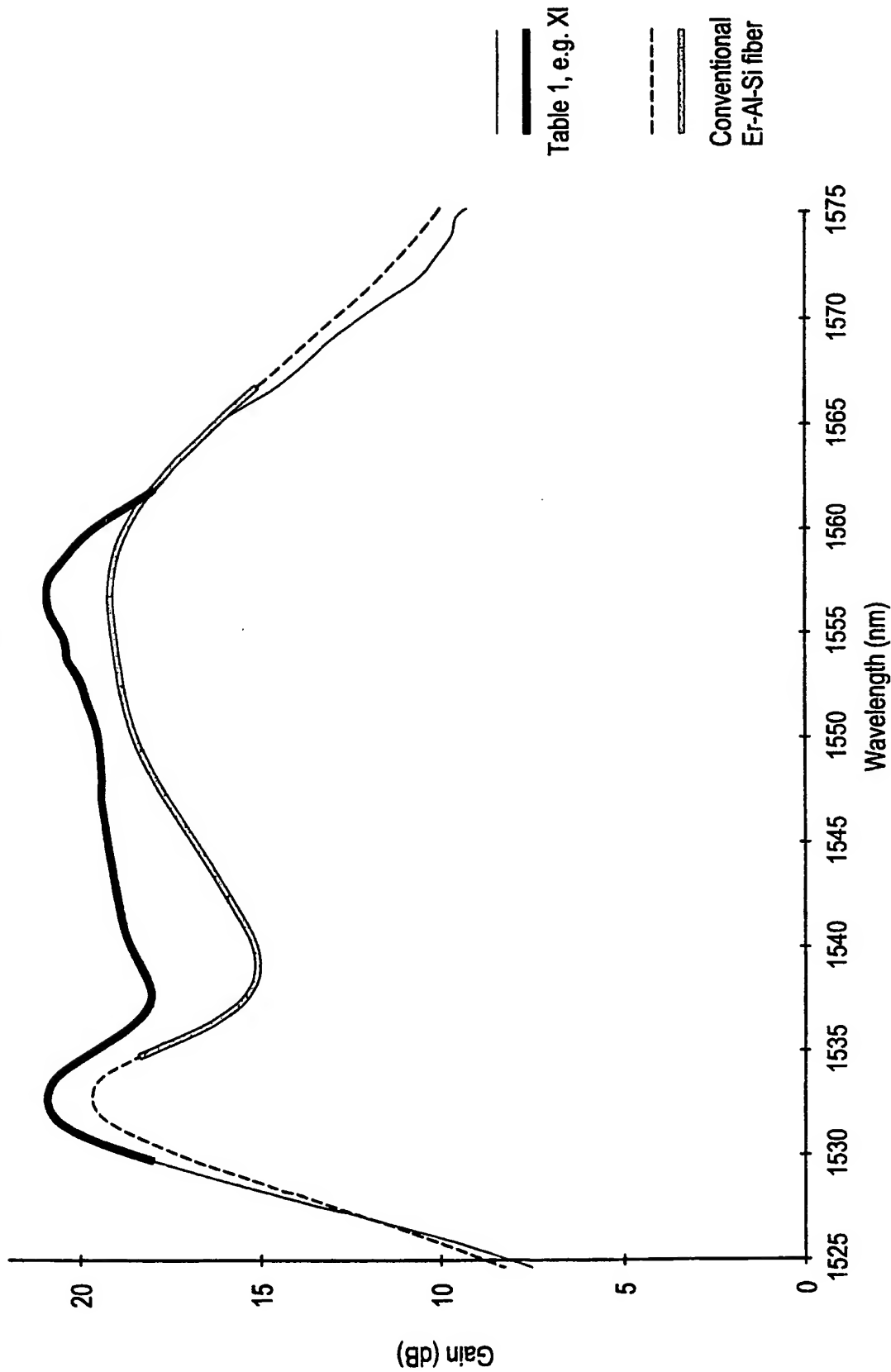
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	Al_2O_3	5-40
	Ga_2O_3	5-40
	$\text{RE}_2(1)\text{O}_3$	0-40
	$\text{RE}_2(2)\text{O}_3$	0-1
5	Er_2O_3	0.001-5
	Yb_2O_3	0-5
	PbO	0-15
	RO	0-20
	ZnO	0-10
10	ZrO_2	0-2
	TiO_2	0-2
	Nb_2O_5	0-10
	Ta_2O_5	0-10
	P_2O_5	0-5
15	B_2O_3	0-15
	As_2O_3	0-10
	Sb_2O_3	0-20
	Na_2Cl_2	0-10
	Bi_2O_3	0-5, and
20	up to 15 weight % fluorine in the form of at least one of a fluorinated component of the glass composition and a batch constituent selected from a group consisting of at least one of AlF_3 , REF_3 , NH_3F_2 , NaF , Na_2SiF_6 , Na_3AlF_6 , where $\text{RE}(1)$ is at least one of Y, La, Gd, and Lu; $\text{RE}(2)$ is at least one of Ce, Pr, Nd, Sm, Eu, Tb, Dy, Ho, and Tm; R is at least one of Ba, Ca, Mg, and Sr; $(\text{SiO}_2 + \text{GeO}_2)$ is in the range (40-90); and $(\text{Al}_2\text{O}_3 + \text{Ga}_2\text{O}_3) > (\text{RO} + \text{"alk"}_2\text{O} + \text{RE}_2\text{O}_3)$ where "alk" is at least one of Li, Na, K, Cs, and Rb.	
25		
30	14. The method of claim 13 in which the cladding has a composition consisting essentially, in mole %, of:	
	SiO_2	90-100

	B_2O_3	0-10
	P_2O_5	0-10
	Al_2O_3	0-10
	GeO_2	0-10
5	SiF_4	0-10.

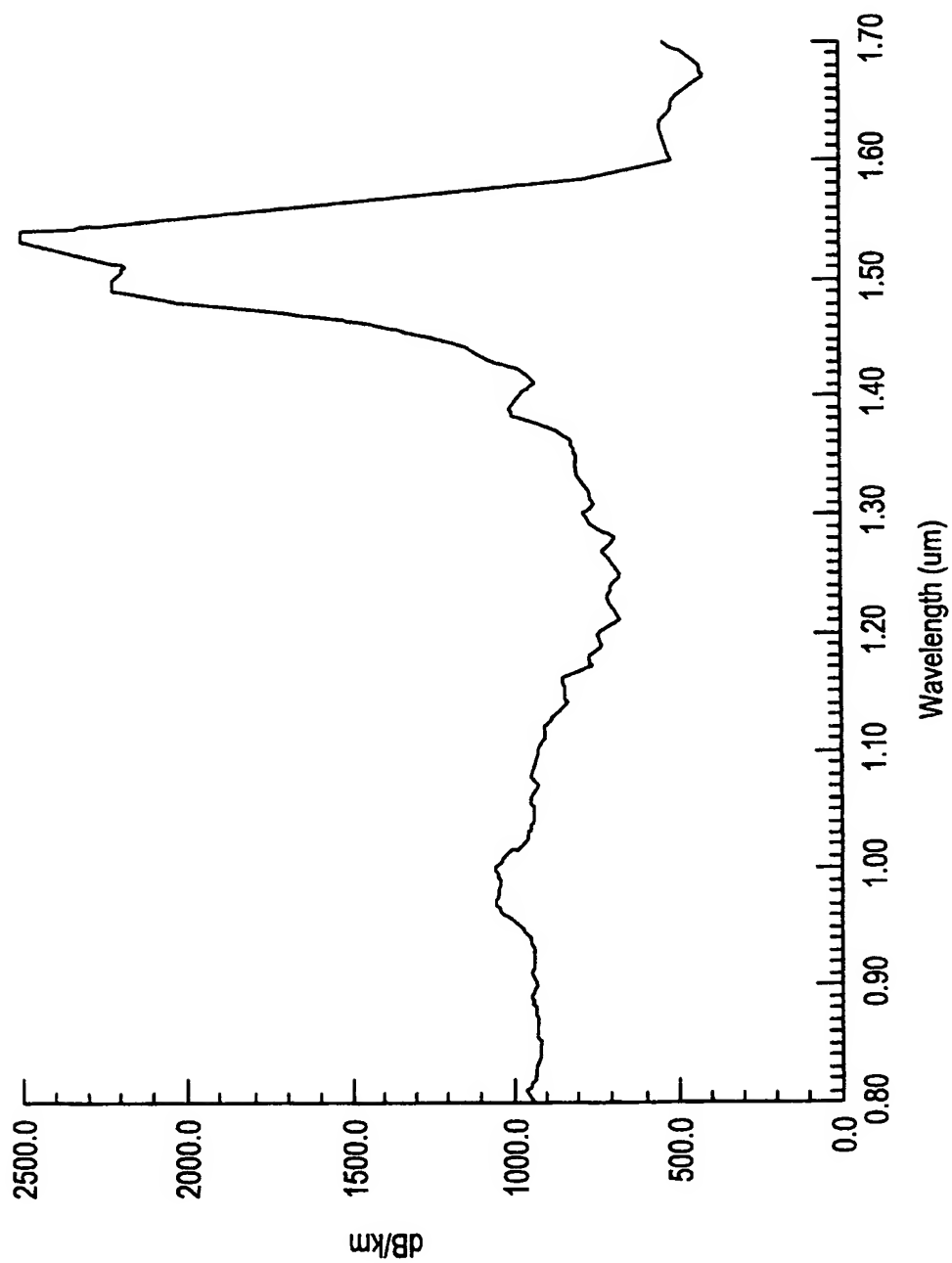
15. The method of claim 12 in which the cladding structure is a tube that is not sealed at any part thereof that is not the drawing end.
- 10 16. The method of claim 12 in which the core cullet is a glass-ceramic.
17. The method of claim 12 in which the core cullet is a superconductor.
18. An optical signal amplifier made according to the method of claim 12.
- 15 19. An optical isolator made according to the method of claim 12.
20. A laser made according to the method of claim 12.
- 20 21. An optical filter made according to the method of claim 12.
22. A single mode optical waveguide fiber made according to the method of claim 12.
- 25 23. A multimode optical waveguide fiber made according to the method of claim 12.

FIG. 1



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FIG. 2



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FIG. 3

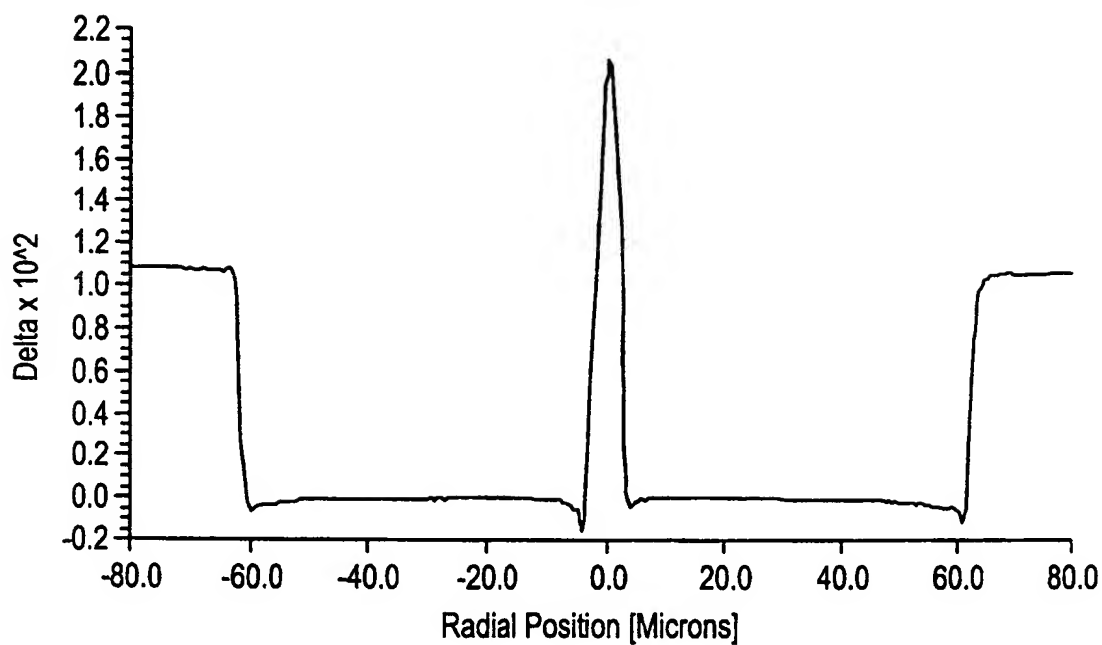


FIG. 4

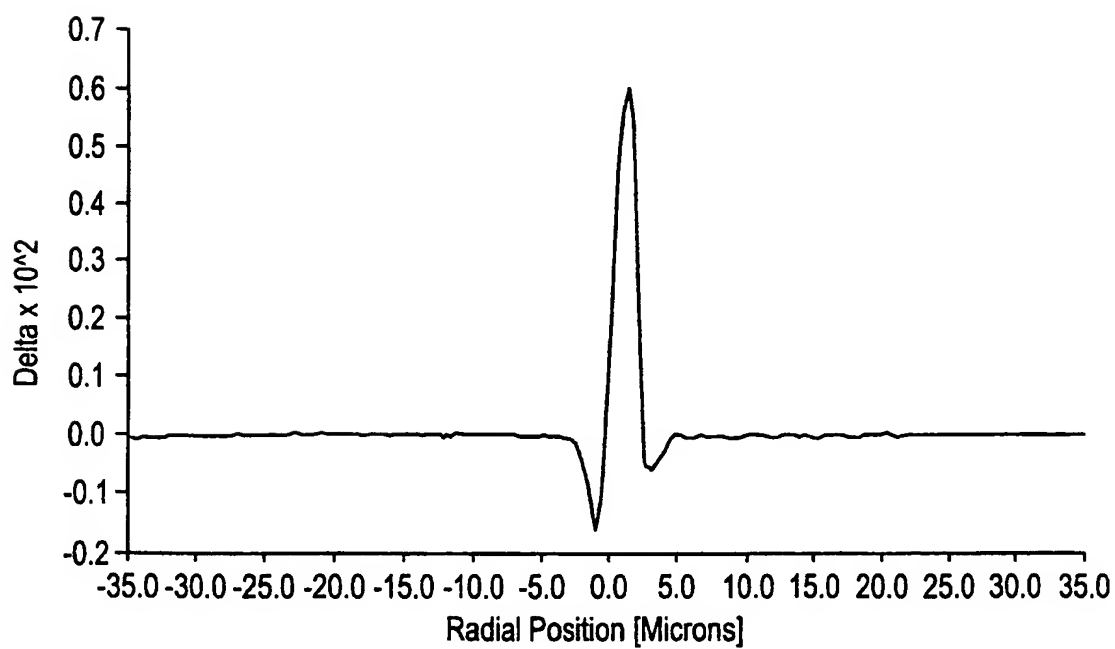
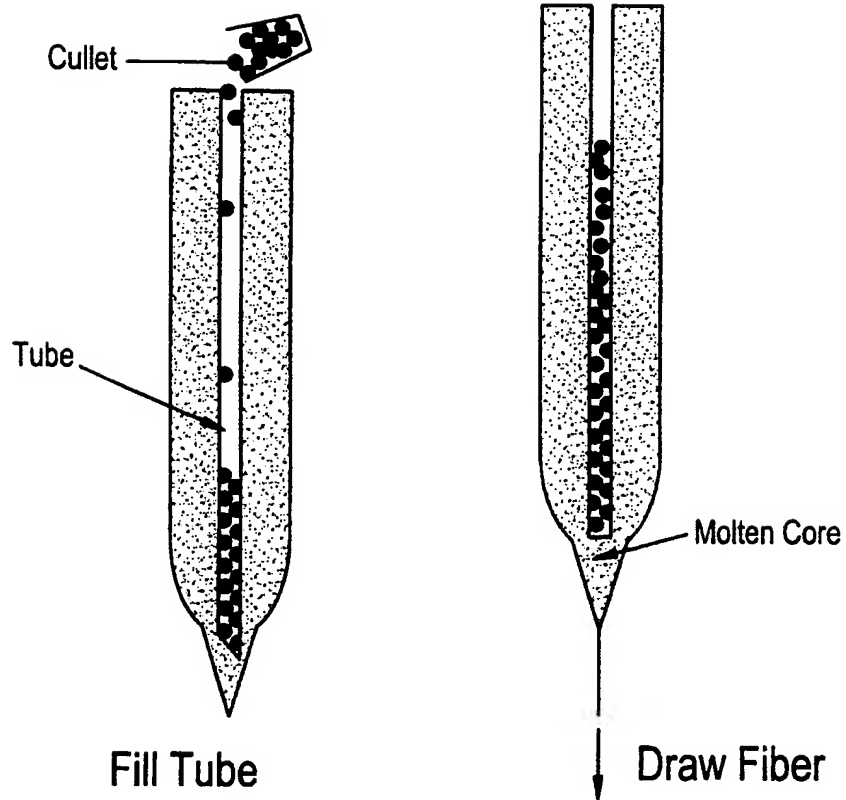


FIG. 5



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/12336

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : CO3C 13/04; CO3B 37/023; GO2B 6/02

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 501/37, 41, 42, 44, 50, 64, 73, 78; 385/141, 142, 144; 359/341, 343; 65/435

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,573,571 A (KOPYLOV et al) 12 November 1996 (12-11-96), see column 3, lines 15-51.	12
A,P	US 5,747,397 A (McPHERSON et al) 05 May 1998 (05-05-98).	1-11
A	US 5,253,322 A (ONISHI et al) 12 October 1993 (12-10-93).	1-11
A	US 4,962,995 A (ANDREWS et al) 16 October 1990 (16-10-90).	1-11
A	US 4,936,650 A (AINSLIE et al) 26 June 1990 (26-06-90).	1-11

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

10 SEPTEMBER 1998

Date of mailing of the international search report

OCT 13 1998

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US98/12336

A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

501/37, 41, 42, 44, 50, 64, 73, 78; 385/141, 142, 144; 359/341, 343; 65/435

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